

KOKAI PATENT APPLICATION NO. SHO 61-277114

**PRODUCTION OF CONDUCTIVE LAMINATE**

[Translated from Japanese]

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## PRODUCTION OF CONDUCTIVE LAMINATE

*[Dohdensei sekisohtaino seizoh houhoh]*

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*[There are no amendments to this patent.]*

## Specification

## 1. Title of the invention

Production of a conductive laminate

## 2. Claim of the invention

In the manufacture of a conductive laminate where a transparent conductive film mainly comprising an indium oxide layer is formed on an organic polymer molding, a method of manufacturing a conductive laminate characterized by the fact that a non-cured layer mainly comprising an organic silicon compound (B), a layer mainly comprising indium lower oxide (C), and a non-cured layer mainly comprising an organic silicon compound (D) are laminated

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sequentially onto the surface of an organic polymer molding (A), and a heat-treatment is provided for the aforementioned laminate in an oxidizing atmosphere to convert the layer mainly comprising indium lower oxide (C) into a transparent conductive layer (C) mainly comprising indium oxide and at the same time, curing is performed for layers (B) and (D) comprising organic silicon compounds.

## 3. Detailed description of the invention

## [Application field]

The present invention pertains to a conductive laminate and the invention further pertains to a method of manufacturing an organic polymer molding having a transparent conductive layer with high strength.

## [Prior art]

With the arrival of the super information society, development of components and equipment utilizing light and electronics is increasing. Furthermore, with the widespread use of microcomputers, the cutting-edge technology for computer peripheral equipment is remarkable. As an input device for the aforementioned computers, development of transparent switch is making progress. As an embodiment of the structural component, a transparent electrode utilizing an organic polymer molding substrate is used and high durability and high reliability are required for application as a switch. Furthermore, the aforementioned transparent electrode is used for liquid crystal display devices, electroluminescence displays, etc. used as output devices, and high durability and high reliability are required for those purposes as well.

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A conductive laminate where a transparent conductive film is provided on the surface of an organic polymer molding (film, in many cases) has many advantages such as high transparency, flexibility, and processability; however, in comparison to conductive glasses, adhesion between the transparent conductive layer and organic polymer molding, mechanical properties such as abrasion resistance, etc. are inferior. As a means to eliminate the aforementioned problems, a

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method in which an inorganic silicon or silicon compound (oxide, nitride, etc.) thin film is provided on a polymer film ahead of time and a transparent conductive layer is subsequently formed (for reference, see Japanese Kokai [Unexamined] Patent Application No. Sho 52-67647) has been proposed. When a silicon thin film is provided, the surface of the polymer film becomes similar to that of the glass substrate and an increase in adhesive strength between the transparent conductive layer and polymer film can be achieved, but the degree of improvement is a mere 2 to 3 times at most. When the substrate is glass, a method where a silicon dioxide film is provided on an indium oxide type film at a substrate temperature in the range of 350°C to 500°C to prevent change in indium oxide type transparent conductive film has been proposed (for reference, see Japanese Kokoku [Examined] Patent Application No. Sho 49-18446 and Japanese Kokai [Unexamined] Patent Application No. Sho 53-81144), a method where a solution mainly comprising silanol  $\text{Si}(\text{OH})_4$  is coated onto a metal indium film and baked in air at a temperature in the range of 350-400°C to convert the metal indium into an indium oxide transparent conductive film and to form an  $\text{SiO}_2$  layer onto the transparent conductive film at the same time (for reference, see Japanese Kokai [Unexamined] Patent Application No. Sho 54-25493 for reference), etc. are being proposed. An increase in mechanical properties is expected in the aforementioned method, but a high substrate temperature is required for the aforementioned method and the method cannot be used for a conductive laminate comprising a substrate having a low heat-resistance such as an organic polymer molding. Also, in the case of a flexible substrate, a method where a silicon oxide protective layer is provided for a transparent conductive layer comprising a metal oxide for an increase in abrasion resistance is being proposed (for reference, see Japanese Kokai [Unexamined] Patent Application No. Sho 53-67408). In the aforementioned method, heating of the substrate is not especially provided and a silicon oxide layer is formed, and the silicon oxide layer is hard but is also brittle and cracking or peeling of the film occurs and production of a conductive laminate having flexibility and abrasion resistance is not possible.

As a result of much research conducted by the present inventors on a superior conductive

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organic polymer molding having high adhesion as well as abrasion resistance, the inventors discovered that the target performance could be achieved in a conductive laminate in which silicon compound layer (B) mainly comprising an organic silicon compound, transparent conductive layer (C) comprising a metal oxide and silicon compound (D) mainly comprising an organic silicon compound are successively laminated onto the surface of organic polymer molding (A) (for reference, see Japanese Kokai [Unexamined] Patent Application No. Sho 57-159645).

A superior abrasion resistance can be achieved in the aforementioned conductive laminate when used as a leader tape but the abrasion resistance remains insufficient to be used as a transparent switch, which is the target of the present invention.

[Purpose of the invention]

The present invention is based on the above-mentioned background and the purpose of the present invention is to provide a method of manufacturing a conductive laminate having superior durability and reliability.

[Structure of invention]

The aforementioned purpose can be achieved by the invention described below. Namely, the present invention is a method of manufacturing a conductive laminate characterized by the fact that a non-cured layer mainly comprising an organic silicon compound (B), a layer mainly comprising indium lower oxide (C), and a non-cured layer mainly comprising organic silicon compound (D) are laminated sequentially onto the surface of an organic polymer molding (A), and a heat-treatment is provided for the aforementioned laminate in an oxidizing atmosphere to convert the layer mainly comprising indium lower oxide (C) into a transparent conductive layer (C) mainly comprising indium oxide and at the same time, curing is performed for layers (B) and (D) comprising organic silicon compounds in the manufacture of a conductive laminate where a transparent conductive layer mainly comprising an indium oxide layer on an organic polymer molding.

The invention is explained in detail below.

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It is disclosed that organic silicon compound has high affinity with both an inorganic phase and an organic phase and is capable of increasing adhesion between organic polymer molding (A) and transparent conductive phase (C) and that a significant increase in abrasion resistance without losing flexibility of the conductive laminate achieved when transparent conductive layer (C) is covered with an organic silicon compound in Japanese Kokai [Unexamined] Patent Application No. Sho 57-159645 by the present inventors. However, when used as the target transparent switch of the present invention, abrasion resistance is insufficient.

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A further study on the cause of the aforementioned problem found that curing of the layer comprising an organic silicon compound appeared to be insufficient. Therefore, when a heat-treatment was provided for the layer after lamination in an attempt to cure the layer comprising an organic silicon compound, a sharp increase in resistance of the transparent conductive layer was observed and it was found to be unsuitable for a transparent switch. As a cause for the aforementioned problem, it was hypothesized that the transparent conductive layer (C) was oxidized by oxygen permeating the layer comprising the non-cured organic silicon compound during the course of the heat-treatment. Thus, the present inventors focused on the oxygen permeability of the layer comprising the non-cured organic silicon compound. In other words, the present inventors found an indium lower oxide layer (C) was oxidized by oxygen permeating the layer and converted to a transparent conductive layer (C) comprising indium oxide and curing of the layers (B) and (D) comprising organic silicon compound could be achieved at the same time when a non-cured layer mainly comprising an organic silicon compound (B), a layer mainly comprising indium lower oxide (C), and a non-cured layer mainly comprising organic silicon compound (D) were laminated sequentially onto the surface of an organic polymer molding (A), and a heat-treatment was provided for the aforementioned laminate, and as a result, the present invention was accomplished.

According to the method of the present invention, it is possible to laminate a thin film

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having a sandwich structure where a transparent conductive layer (C) having high transparency and conductivity is sandwiched between layers (B) and (D) comprising an organic silicon compound and applied onto an organic polymer molding (A). The conductive laminate of the present invention has high adhesion between the layers and the layer comprising an organic silicon compound is thoroughly cured; thus, a transparent conductive layer with an high reliability and high wear resistance can be achieved.

The organic polymer compound comprising the organic polymer molding (A) in the present invention is not especially limited as long as an organic polymer compound having high heat-resistance is used, and in general, heat-resistance of 100°C or higher, preferably, 130°C or higher, is desirable, and for example, polyimide, polyether sulfone, polysulfone, polyhydantoin, polyethylene terephthalate, polyethylene-2,6-naphthalene dicarboxylate, polydiallyl phosphate, polycarbonate and other polyester type resins, and furthermore, aromatic polyamide, polyamide, polypropylene, cellulose triacetate, etc. can be mentioned. Needless to say, the aforementioned compounds can be used as homopolymers, copolymers, or blend polymers.

The shape of the aforementioned molding of organic polymer compound is not especially limited, and in general, either sheet or film is desirable, and film, in particular, is especially desirable since winding is possible and continuous production is made possible. When used as a film, the thickness of the film is preferably in the range of 6-500  $\mu\text{m}$ , and especially, in the range of 12-200  $\mu\text{m}$ .

Furthermore, a suitable amount of pigments may be added or surface treatment, for example, a sand matting treatment, etc. may be provided, as well.

And furthermore, the aforementioned film may be used alone or as a laminate.

The organic silicon compound that comprises layer (B) of the present invention is an organic metal compound having a group having affinity with or forming a chemical bond with the inorganic phase and a group having affinity with or forming a chemical bond with the organic phase at the same time, and is a organic metal compound containing silicon (Si).

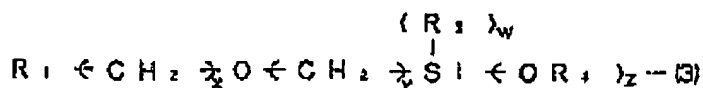
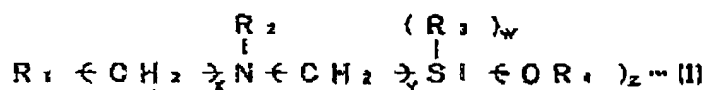


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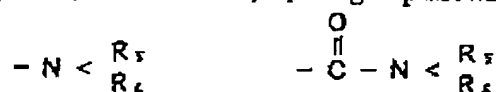
For the aforementioned group having affinity with or forming chemical bonds with the inorganic phase, groups that can be converted to a hydroxyl group as a result of a hydrolysis reaction, for example, alkoxy groups, in particular, alkoxy groups with 4 or fewer carbon atoms, halogen atoms, tert-butyl peroxy groups, and acyl groups can be mentioned, and for the aforementioned group having affinity with or forming chemical bonds with the organic phase, lower alkyl groups, phenyl groups, (meth)acryloxy groups, (meth)acryloxy propyl groups, vinyl groups, epoxy groups, and substituted or non-substituted amino groups can be mentioned.

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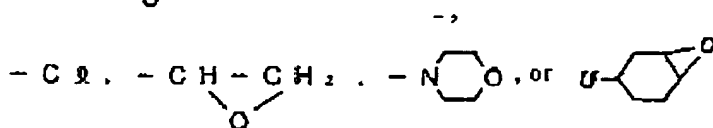
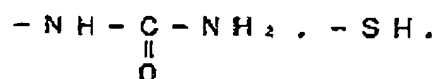
As desirable compounds, the compounds shown in general formulas (1)-(3) shown below:



[where, in the formula,  $R_1$  is a group shown in the formulas below



[provided that in the formula,  $R_5$  and  $R_6$  are each independently a group selected from hydrogen atoms, alkyl groups with 1-4 carbon atoms, hydroxy alkyl groups, phenyl groups, allyl groups ( $-CH_2-CH=CH_2$ ) and carboxy methyl groups ( $-CH_2-COOH$ ).],



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$R_2$  is either a hydrogen atom or an alkyl group with 1-12 carbon atoms;  $R_3$  and  $R_4$  are each independently an alkyl group with 1-4 carbon atoms;  $x$  and  $y$  are each independently an integer in the range of 1-12;  $w$  is either 0 or an integer of 1-2;  $xz$  is an integer in the range of 1-3, and  $w+z=3$ .] and compounds shown in general formula (4)



[where, in the formula,  $R$  is an organic group such as methyl, ethyl, propyl, butyl, vinyl, phenyl, methacryloxy, or methacryloxy propyl;  $X$  is halogen atom, alkoxy group, tertiary butyl peroxy group, or acryl group;  $m$  is an integer in the range of 1 to 3 and satisfies  $n+m=4$ .]

and oligomers produced by hydrolysis of the aforementioned compounds can be used effectively.

Among those listed above, those containing amino group ( $-NH_2$ ) as a functional group are desirable, and for example, one or more of monomers of  $NH_2-(CH_2)_3-Si-(OCH_3)_3$  and/or  $NH_2-(CH_2)_3-Si(CH_3)-(OCH_3)_2$ , and/or  $NH_2-(CH_2)_3-Si(CH_3)-(OC_2H_5)_2$ , and/or  $NH_2-(CH_2)_2-NH-(CH_2)_3-Si-(OCH_3)_3$ , and/or  $NH_2-(CH_2)_2-NH-(CH_2)_3-Si-(OC_2H_5)_3$ , and/or  $NH_2-(CH_2)_2-NH-(NH_2)_3-Si(CH_3)-(OCH_3)_2$ , and/or  $NH_2-(CH_2)_2-NH-(CH_2)_3-Si(CH_3)-(OC_2H_5)_2$  and/or oligomers with an association degree of 10 or less formed as a result of hydrolysis of the aforementioned monomers are especially desirable.

The aforementioned organic silicon compound may be used in the form of a mixture with other organic metal compounds, for example, organic titanium compounds such as titanium alkyl esters, organic zirconium compounds such as zirconium alkyl esters, and furthermore, an appropriate amount of curing catalysts, adhesive enhancers, wetting agents, plasticizers, various stabilizers, flame retardants, antioxidants, lubricants, foaming agents and/or thickeners may be mixed as needed.

The aforementioned compound may be used as is or after dissolving in a solvent. For examples of the aforementioned solvents, one or mixtures of methanol, ethanol, isopropanol, n-butanol, toluene, ethyl acetate, ligroin, ethyl cellosolve, etc. can be mentioned.

The thickness of the layer (B) mainly comprising the aforementioned organic silicon

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compound is not especially limited and a thickness in the range of 0.01-1  $\mu$  is desirable. From the standpoint of abrasion resistance and optical properties, a thickness in the range of 0.01-0.1  $\mu$  is further desirable. When the thickness is 0.01  $\mu$  or below, formation of continuous film is less likely to be achieved, and the initial purpose cannot be achieved. On the other hand, when the thickness exceeds 1  $\mu$ , formation of cracks or loss of plasticity of the organic polymer molding occurs.

Upon coating of the aforementioned organic silicon compound, known coaters and coating methods such as doctor knife, bar coater, gravure roll coater, curtain coater, and knife coater, spray coating, dip coating, etc. may be used according to the shape and properties of the organic polymer molding and organic silicon compound.

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After coating the aforementioned organic silicon compound onto the organic polymer molding, the solvent is evaporated to form a film material.

Furthermore, as a method used for formation of the layer mainly comprising an indium lower oxide used in the present invention, a known method, for example, vacuum deposition method, sputtering method, ion plating method, etc. can be mentioned.

For the vacuum deposition method, an alloy mainly comprising indium or a molding mainly comprising indium oxide can be used as the deposition source. In the former case, a reactive gas such as oxygen gas is introduced to the vacuum tank and reactive deposition is performed. In the latter case, deposition is performed with or without a trace amount of reactive gas such as oxygen gas introduced to the vacuum tank.

For the heating means used for the deposition material, known methods such as resistance heating, high frequency heating, and electron beam heating can be used, and electron beam heating is further desirable to produce a uniform film at a high-speed.

In the sputtering method, an alloy mainly comprising indium or a sinter mainly comprising indium oxide can be used as the deposition source. In the former case, an inert gas such as argon

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and a reactive gas such as oxygen are introduced to the vacuum tank and reactive sputtering is performed. In the latter case, an inert gas such as argon alone or an inert gas such as argon mixed with a trace amount of reactive gas such as oxygen gas is used and sputtering is performed. For the aforementioned sputtering method, known methods such as DC or high-frequency bipolar sputtering, DC or high-frequency magnetron sputtering and ion beam sputtering method may be used. Among those listed above, magnetron sputtering is further desirable since plasma the impact on the substrate is low and high-speed film formation is possible.

Furthermore, for the ion plating method, an alloy mainly comprising indium or a molding mainly comprising indium oxide can be used as the deposition source. In the former case, an inert gas such as argon alone or an inert gas such as argon mixed with a trace amount of reactive gas such as oxygen is introduced to the vacuum tank and reactive ion plating is performed. In the latter case, an inert gas such as argon alone or an inert gas such as argon mixed with a trace amount of reactive gas such as oxygen gas is used.

In this case, in the ion plating method, film formation is achieved as vaporized particles and/or a portion of the induction gas is being ionized and for the ionization method, a method where DC, AC, high-frequency waves, microwaves, etc. are applied can be mentioned. Furthermore, a method where an ionizing electrode is provided at or near the deposition source and induction gas is omitted is known as well.

After forming layer (D) described below, the aforementioned layer (C) mainly comprising an indium lower oxide is converted to transparent conductive layer (C) as a result of a heat-treatment performed under an organic atmosphere.

The transparent conductive layer (C) used in the present invention is a layer mainly comprising an indium oxide. Basically, the indium oxide is a transparent electrically insulating material but become semiconductors when (1) an trace amount of impurities are included, (2) slightly lacks oxygen, etc. As a desirable semiconductor metal oxide, for example, indium oxide containing tin or fluorine as impurities can be mentioned. Furthermore, a layer comprised of

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indium oxide containing 2-20 wt% of tin oxide is especially desirable.

In order to achieve a sufficient conductivity, it is desirable when the film thickness of the aforementioned oxide film is at least 30 Å and at least 50 Å is further desirable. And furthermore, in order to produce a film having a sufficient transparency, a film thickness of not more than 500 Å is desirable, and not more than 400 Å is further desirable.

The organic silicon compound comprising layer (D) of the present invention is one or more compounds selected from organic silicon compounds comprising layer (B) of the present invention, furthermore, the formation method described for formation of the aforementioned layer (B) may be used as is. And furthermore, the same organic silicon compound that comprises layer (B) or different compounds may be used or a part may be the same as layer (B).

The thickness of the layer (D) mainly comprising the aforementioned organic silicon compound is not especially limited and a thickness in the range of 0.01-0.5 μ is desirable. From the standpoint of abrasion resistance and optical properties, a thickness in the range of 0.01-0.1 μ is further desirable. When the thickness is below 0.01 μ, formation of continuous film is less likely to be achieved, and the initial purpose cannot be achieved.

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On the other hand, when the thickness exceeds 0.5 μ, formation of cracks; loss of conductivity on the surface, or loss of plasticity of the organic polymer molding occurs.

After sequentially depositing each layer of (B), (C) and (D) onto organic polymer molding (A) as described above, a heat-treatment is provided for the aforementioned laminate under an oxygen atmosphere, layer (C) mainly comprising an indium lower oxide is converted to transparent conductive layer (C) and layers (B) and (D) comprising an organic silicon compound are cured at the same time.

In this case, the aforementioned oxygen atmosphere means an atmosphere where oxygen required for converting the layer mainly comprising indium lower oxide into an indium oxide layer is included, and an inert gas may be included, as needed, and for example, ambient pressure

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atmosphere containing an oxygen gas and/or ozone, low-pressure atmosphere containing oxygen gas and/or oxygen plasma, high-pressure atmosphere containing oxygen gas and/or ozone, etc. can be mentioned, and ambient pressure atmosphere containing an oxygen gas and/or ozone is further desirable and air or air containing ozone is especially desirable. Furthermore, a heat-treatment temperature in the range of 100-250°C is desirable and in the range of 130-200°C is further desirable. When the aforementioned temperature is 100°C or below, conversion to indium oxide having high transparency cannot be achieved and it is not suitable for curing of the aforementioned organic silicon compound. On the other hand, when the aforementioned temperature exceeds 250°C, deformation or cracks are formed in the organic polymer molding. It should be noted that the heat-treatment time is determined experimentally according to the heat-treatment temperature, composition of layers, etc., and a sufficient time for the indium lower oxide layer to be converted into a transparent indium oxide layer and curing of the organic silicon compound is required and in general, several tens of minutes to several tens of hours is required.

## [Effect of the invention]

As explained above, production of a conductive laminate having excellent wear resistance and reliability and can be used for transparent switch is made possible according to the method of the present invention.

Furthermore, the conductive laminate produced in the present invention can be effectively used as electrophotography, antistatic materials, surface heating units, solid display, optical memory, photo-electric conversion elements, optical communication, optical information processing, solar energy materials in addition to the aforementioned transparent switch.

The present invention is further explained in specific terms with working examples below.  
[Working Examples 1 and Comparative Examples 1 and 2]

A mix alcohol solution of ethanol, butanol and isopropanol containing 1.0 wt% of a condensate produced by a hydrolysis reaction of  $\gamma$ -aminopropyl triethoxysilane was coated onto both surfaces of a polyethylene terephthalate film (A) with a thickness of 100  $\mu\text{m}$  by a gravure

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coater as a organic silicon compound and drying was performed for 1 minute at a temperature of 150°C to produce a layer (B) comprising an organic silicon compound. The thickness of the aforementioned layer (B) was 300 Å.

Furthermore, the intermediate laminated film laminated with the aforementioned layer (B) was placed inside a vacuum deposition device, an ion bombardment treatment was provided for one surface of the aforementioned intermediate laminated film based on Ar glow discharge, evaporation was performed for a mixture comprising 95 wt% of  $\text{In}_2\text{O}_3$  and 5 wt% of  $\text{SnO}_2$  under  $2 \times 10^{-4}$  Torr so as to form a black colored indium-tin lower oxide layer (C) onto the aforementioned layer (B). The film thickness of layer (C) was 300 Å.

The intermediate conductive film laminated with the aforementioned layer (C) is hereinafter referred to as film (a).

A mixed solution of ethanol, butanol and isopropanol containing 1.5 wt% of the aforementioned organic silicon compound was coated onto layer (C) of the aforementioned film (a) by gravure coating, and dried for 1 minute at a temperature of 150°C to produce layer (D) mainly comprising an organic silicon compound. The film thickness of layer (D) is 500 Å.

Furthermore, as a heat-treatment under an oxidizing atmosphere, a thorough heat-treatment was provided by a hot air dryer kept at a temperature of 150°C for at least several hours so as to convert the indium-tin lower oxide layer (C) into a transparent conductive layer (C) and to cure layers (B) and (D) comprising an organic silicon compound, and finally, to produce the target conductive laminate (Working Example 1).

[p. 7]

Furthermore, for comparison, first, heat-treatment was provided for the aforementioned film (a) in a hot air dryer to convert indium-tin lower oxide layer (C) and to cure layer (B) and to produce a conductive laminate without layer (D) (Comparative Example 1).

Then, an organic silicon compound was coated onto the aforementioned conductive laminate of Comparative Example 1 as in the case of Working Example 1 and dried to produce a

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layer mainly comprising an organic silicon compound (D) and having a thickness of 500 Å on the transparent conductive layer (C) to produce a transparent conductive laminate having the layer structure described in Working Example 1 (Comparative Example 2).

Furthermore, for samples of Working Example 1 and Comparative Examples 1 and 2, abrasion resistance was examined. In other words, each sample was applied to an acrylic sheet with a thickness of 3 mm with an adhesive tape with the conductive layer faces upward direction. After stabilizing the aforementioned test sample onto the testing board and the aforementioned conductive layer was rubbed with a 4 mm steel ball covered with gauze. The load applied was 110 g and sliding speed was 15 mm/sec. The abrasion resistance is defined as the number of times sliding (number of reciprocating motions) where the surface electrical resistance becomes 1.1 times the value before sliding.

Furthermore, measuring was performed for surface electrical resistance and light transmittance at 550 nm for each sample. And the results obtained are shown in Table I below along with the results of the aforementioned abrasion resistance.

As shown in the Table, excellent abrasion resistance of several tens of times that of the comparative example was achieved in the conductive laminate (Working Example 1) produced by the method of the present invention.

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Table I

Sample No.	Resistance (Ω/square)	Transmittance (%)	Abrasion resistance (number of times sliding)	Remarks
Working Example 1	290	85	450-500	---
Comparative Example 1	290	84	1	Without layer (D)
Comparative Example 2	290	85	5-10	---



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[Comparative Examples 3 and 4]

A polyethylene terephthalate film with a thickness of 100  $\mu\text{m}$  having layer (B) with a thickness of 300 Å produced by coating and drying the organic silicon compound solution as in the case of Working Example 1 was placed inside a sputtering device and exhaust was performed to  $5 \times 10^{-6}$  Torr and a mixed gas of argon and oxygen (oxygen content 25 vol%) was introduced, the pressure was maintained at  $5 \times 10^{-3}$  Torr and DC reactive sputtering was performed using indium-tin alloy target (5 wt% of tin) to form transparent conductive layer (C) with a thickness of 300 Å on the layer (B).

Furthermore, the same organic silicon compound solution was coated onto the aforementioned transparent conductive layer (C) as in the case of Working Example 1 and dried to form layer (D) with a thickness of 500 Å so as to produce a transparent conductive layer having the layer structure described in working example 1 (Comparative Example 3).

And furthermore, a heat-treatment was provided for the aforementioned transparent conductive layer produced in working example 3 by a hot air dryer kept at a temperature of 150°C as in the case of Working Example 1 to produce a transparent conductive layer with cured layers (B) and (D) (Comparative Example 4).

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Surface electrical resistance, light transmittance at 500 nm and abrasion resistance of Comparative Examples 3 and 4 are shown in Table II below.

As shown in the Table, abrasion resistance is inadequate, and an increase in resistance is observed in Comparative Example 4 and cannot be used as a switch.

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Table II

Sample No.	Resistance ( $\Omega$ /square)	Transmittance (%)	Abrasion resistance (number of times sliding)	Remarks
Comparative Example 3	380	82	5-10	—
Comparative Example 4	1480	84	30-40	High resistance, not suitable for switch

Note) The evaluation method used for the abrasion resistance is the same as for Working Example 1.

[Working Example 2 and Comparative Examples 5 and 6]

Instead of the aforementioned organic silicon compound solution, a mixed alcohol solution comprising methanol, ethanol, butanol and isopropanol produced as a condensate based on a hydrolysis reaction of N- $\beta$ -(aminoethyl)- $\gamma$ -aminopropyl-trimethoxy silane and production was done as in Working Example 1 and Comparative Examples 1 and 2 so as to produce the corresponding Working Example 2 and Comparative Examples 5 and 6. It should be noted that the film thickness of layer (B), layer (C) and layer (D) of the aforementioned samples was 200 Å, 260 Å, and 500 Å, respectively.

The abrasion resistance of the aforementioned samples was measured by a different method from those of previous method. A conductive laminate was applied to an acrylic sheet with a thickness of 3 mm with the conductive layer faces upward direction, a different conductive laminate was applied onto the aforementioned conductive laminate with a spacer having a thickness of 100  $\mu$ m with the conductive layer facing in the downward direction (that is, in such

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a manner that conductive layers face each other with a 100  $\mu\text{m}$  spacer between them) and bonded. In other words, when pressure is applied to the upper conductive laminate (namely, opposite surface from the conductive layer), the aforementioned conductive layers come in contact with one another.

After fastening the aforementioned test samples onto a testing board, steel ball with a diameter of 4 mm was rolled on the upper conductive laminate. The load applied was 110 g and sliding speed was 15 mm/sec. The abrasion resistance is defined as the number of times sliding (number of reciprocating motions) until the surface electrical resistance becomes 1.1 times the value before sliding.

The measured result of abrasion resistance of each of the aforementioned samples is shown in Table III along with surface electrical resistance and light transmittance at 500 nm.

As shown in the Table, excellent abrasion resistance of 10 times or higher compared to that of the comparative examples was achieved in the conductive laminate (Working Example 2) produced by the method of the present invention.

Table III

Sample No.	Resistance ( $\Omega/\text{square}$ )	Transmittance (%)	Abrasion resistance (number of times sliding)	Remarks
Working Example 2	340	86	3600-3700	---
Comparative Example 5	340	85	50-100	Without layer (D)
Comparative Example 6	340	86	200-300	---

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